FIRST QUARTERLY REPORT

FOR

THE IMPROVEMENT OF ZINC ELECTRODES FOR ELECTROCHEMICAL CELLS
(12 June 1964 - 12 Sept. 1964)

CONTRACT NO.: NAS5-3908

Prepared by:

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Great Neck, N. Y.

GODDARD SPACE FLIGHT CENTER

Greenbelt, Maryland

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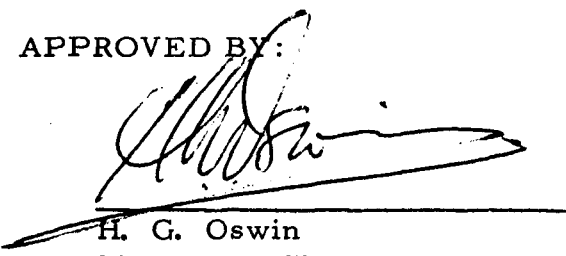(12 June 1964 - 12 September 1964)

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ABSTRACT

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The objective of the work to be conducted under this contract is to determine the factors which govern dendritic shorting, due to zinc, in silver-zinc secondary batteries. It is expected that from a better knowledge of the mechanisms of zinc dendrite growth it will be possible to develop acceptable solutions to the problem and to extend the cycle-life of silver-zinc batteries significantly.

Work projected for this quarter included completion of a survey of the pertinent literature and preliminary experimental study of dendrite formation.

The study to date has comprised cathodic growth and anodic dissolution of zinc dendrites on flat sheet zinc electrodes held horizontally. All experiments have been performed at room temperature under potentiostatic conditions. Parameters varied were, electrolyte and zincate concentrations and potential of the electrode during growth.

The principal conclusion based on these experiments is that there is a definite progression in dendritic form from "mossy" to "acicular" (including intermediate modifications) as the potential of growth is made more cathodic to the experimental reversible potential of the zinc-zincate couple. This progressive modification is specifically a function of potential, rather than of the concentrations of electrolyte or zincate.

Two further observations of interest are that, during anodic dissolution of the dendrites:

1. a highly active zinc surface is formed that is capable of displacing hydrogen from the electrolyte much more rapidly than does smooth zinc, and

2. most of the current during dissolution goes toward reducing the thickness of the individual dendrites rather than toward reducing their length.

Both points may be pertinent to certain known characteristics of poor battery performance.

Work during the next quarter will include determination of the rates of propagation of the various dendritic forms characterized in the present report (e. g. , in the units of mm growth per coulomb zinc deposited). The effects of varying temperature and zinc substrate upon the nature of growth and rates of propagation will also be studied.
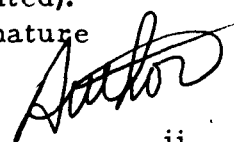
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SECTION I - INTRODUCTION

The rechargeable zinc electrode in alkaline systems is unique among electrodes commonly used in secondary batteries in that the product of discharge (zincate) is extremely soluble in the electrolyte. This leads to problems of recovery and redistribution of the active material during subsequent recharging. The active material is never replaced on the substrate in the original configuration, and repeated charge/discharge cycling often leads to failure of the battery due to the extension of zinc dendrites through the separator materials to the positive plates.

The causes of dendritic growth are not well understood for any metal system, and, in the case of zinc/zincate, no fundamental study of the mechanism of the process has appeared in the literature. A continuing search of the literature since the beginning of the present contract has failed to reveal any publications dealing with this subject, other than that by Mme. Kryukova[1] discussed in the original proposal.

The mechanism of dendrite growth considered most important is that occurring during discharge of the zincate anion ($Zn(OH)_4^{=}$) on the zinc negative plate in the charging cycle. Other possible contributing mechanisms, such as spontaneous recrystallization of the zinc negative plate while the system is in the charged state or an internal self-discharge involving zincate, are not being considered at the moment.

The approach has been, first, to establish the current-voltage characteristics of the $Zn/Zn(OH)_4^{=}/KOH$ system as functions of the concentrations of zincate and potassium hydroxide, and, second, to outline and vary systematically the parameters likely to be important factors determining the growth characteristics of cathodically grown dendrites. These factors are:

1. Concentration of electrolyte.

2. Concentration of zincate (introduced as ZnO).

3. Potential of zinc electrode during growth.

4. Nature of zinc substrate (e. g. , plaque, smooth, etc.)

5. Temperature during growth.

6. Impurities (or additives) in the system.

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1 T. A. Kryukova, <u>Soviet Electrochemistry</u>, Vol. III, Applied, pp 147-151, Consultants Bureau, N. Y. (1961)

7.   (Separator material)[2]

From a practical point of view, certain limits can be placed upon the concentration and temperature ranges of interest. These are:

KOH, 30 - 45 (w) %

$Zn(OH)_4^=$, 0 - 1.1$\underline{M}$ (saturation value in 44 (w)% KOH).

Temperature, 0 - 50°C.

All of the work to date has been carried out potentiostatically on flat plate zinc electrodes at room temperature. The parameters 1 through 3 above have been varied and some striking differences in the nature of dendritic growth have been noted, particularly as a function of parameter 3, the potential of growth.

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2 Not within the scope of this contract.

SECTION II - DISCUSSION

2.1   EXPERIMENTAL METHODS

2.1.1   Materials

Materials of reagent purity were used throughout the work. It is recognized, however, that very small amounts of impurities can markedly affect the nature of electrodeposition of metals. While no specific effects are known at this time, analytical data on each of the three active materials employed thus far in the study are given for possible future reference.

ZnO (Fisher "Certified Reagent")

Semi-quantitative emission spectrum for metals:

Pb	0.001 - 0.003%
Si	0.001 - 0.003%
Cu	0.0004 - 0.0006%
Fe	0.0004 - 0.0006%
Mg	0.0004 - 0.0006%

(No others detected.)

Manufacturer's analysis for non-metals:

Cl^- 0.008%
NO_3^- p.t.
S-containing compounds: 0.003%

Zn (Cast Rod, 1/4" Dia., Fisher)

Semi-quantitative emission spectrum for metals:

Cu	0.001 - 0.003%
Pb	0.001 - 0.003%
Fe	0.0004 - 0.0006%
Ag	0.0004 - 0.0006%

(No others detected.)

KOH (Baker "Analyzed Reagent")

Manufacturer's analysis of lot:

Heavy metals (as Ag)	0.0006%
Fe	0.0003%
Ni	0.001%
Na	0.03%
K_2CO_3	0.65%
Cl	0.003%
N-containing compounds	0.0005%
$PO_4^=$	0.0001%
$SO_4^=$	0.001%

2.1.2   Equipment and Apparatus

Current-voltage data and dendrite growth measurements were obtained
with a conventional three-electrode system in a special observation cell
(described below), in conjunction with a Wenking potentiostat and a
Fluke differential voltmeter. An optical magnification system was
designed and constructed for viewing and photographing the zinc working
electrode during the deposition and dissolution of dendrites. The over-
all arrangement of components is shown in Figure 1 and a photograph of
the optical system in Figure 2.

The photographic apparatus consisted of an Exacta 35 mm camera fitted
with a bellows attachment to which a Gaertner "telemicroscope" was
affixed. The telemicroscope has a focus distance of 4.75" and in
conjunction with the camera, gives an over-all magnification of
approximately 95x on a 4 1/2" x 7" print. The entire photographic
system was mounted to permit measurable degrees of freedom, viz.,
vertical and norizontal.

This apparatus is set on a steel plate supported on six shock mounts.
The cell as well as the photographic apparatus is situated on this
vibrationless plate. Difficulty was encountered, however, in the
photography of the dendrites due to vibration originating in the shutter
mechanism. This was overcome by timing the lights rather than the
shutter. The shutter was opened on time exposure and after the
vibrations had stopped, as indicated by a mercury pool, the lights were
turned on for one second. A darkroom timer (Professional Time-o-
Light) ensured the reproducibility of the exposure light. The small
orifice of the telemicroscope prevents fogging of the film from room
illumination after the shutter is opened prior to illumination of the
electrode.
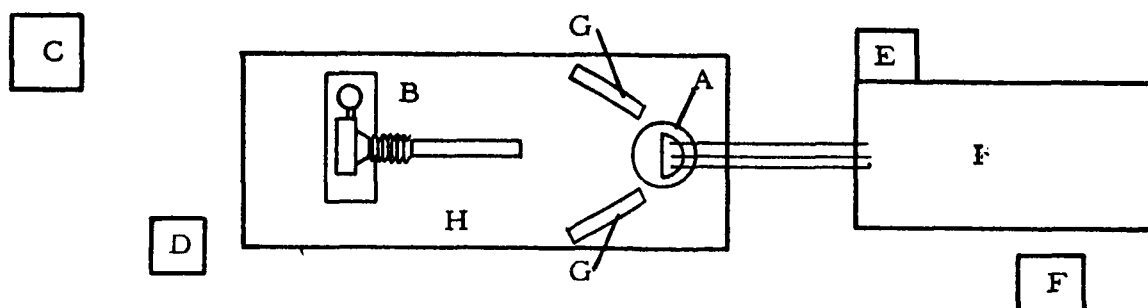
Figure 1. Arrangement of Apparatus (top view)

A.   The electrolysis cell.
B.   Photographic apparatus.
C.   Clock
D.   Light Timer
E.   Fluke differential voltmeter
F.   Potential drive motor
G.   Illuminating lamps
H.   Damped platform
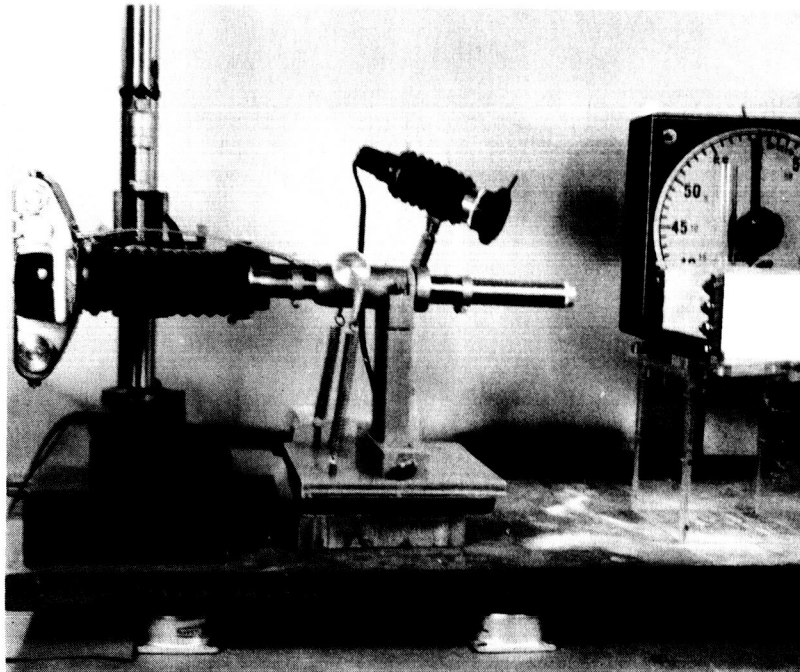I.   Wenking potentiostat

Figure 2.   Viewing System

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The working electrodes for all experiments were zinc of 99.99% purity procured from Fisher Scientific Co. (impurity analysis reported in Section 2.1.1) in the form of 1/4" dia. cast rods. From these, discs of 0.04" thickness were machined and one surface mechanically polished. The discs were set into glass tubing as shown in Figure 3. Epoxy resin was used to insure that the electrolyte did not contact the nickel wire. The epoxy was air-cured for 24 hours after which the entire structure, except for the surface of the electrode, was wrapped with Teflon ribbon. The area of zinc exposed to the electrolyte was 0.68 cm^2. The mounting with the plane of the electrode horizontal was chosen in order to reduce the effects of mass transfer by convection. A Beckman saturated calomel electrode (SCE) was used as a reference electrode. Platinum screen of 80 mesh (1" x 2") was spotwelded to a platinum wire electrode. This was used as the counter electrode. During operation, the counter electrode was separated from the rest of the system by inserting it into a glass tube fitted with a sintered glass disc. The disc permits electrolytic transfer to the main compartment of the cell, but largely prevents diffusion of hydrogen or oxygen, generated at the counter electrode, to the zinc working electrode.

The body of the electrolytic cell (shown in Figure 4) was constructed of Plexiglas, and fitted with a polystyrene window on the front. The viewing window was polished to optical smoothness on both sides to eliminate aberration. Polystyrene had been shown not to be attacked by the electrolyte even up to the boiling point, and to retain its optical clarity under these conditions. The choice of Plexiglas for the main portion of the cell has not proved totally satisfactory, however, as some surface crazing has occurred after long contact with the KOH solutions at room temperature. A new cell is being constructed from Teflon.

2.2　　　　EXPERIMENTAL RESULTS

2.2.1　　　　Current-Voltage Characteristics of the $Zn/Zn(OH)_4^=/KOH$ System

Although in practice, and particularly for satellite application, batteries are charged and discharged under conditions approximating constant current, it was felt that in the present study, little could be learned of the fundamental behavior of the zinc plate by controlling current. In recent years meaningful electrochemical kinetic data has been gathered by controlling electrode potential rather than current density in half-cell experiments. This approach has been taken in the present study though supplementary experiments may be necessary later in which current is controlled and potential monitored.
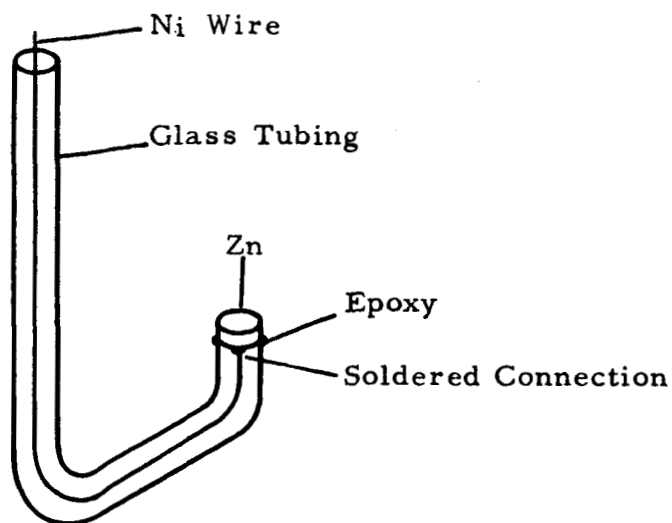
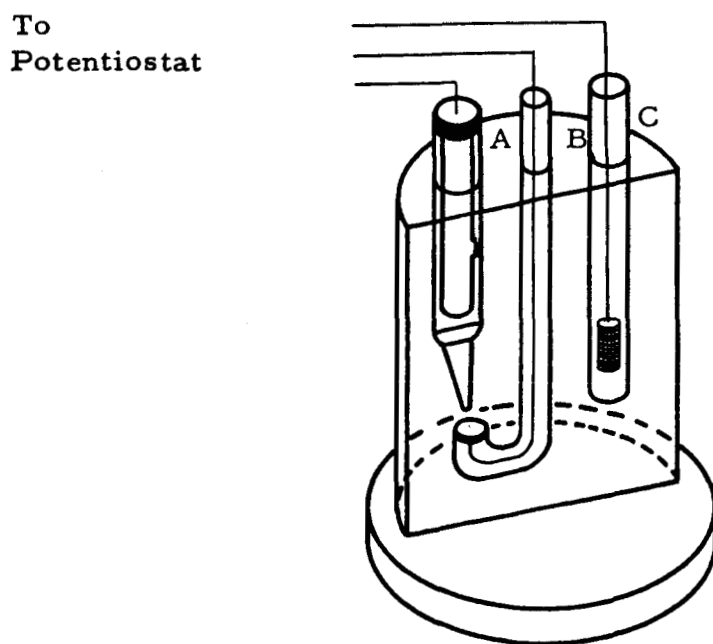Figure 3.   Construction of Zinc Electrodes

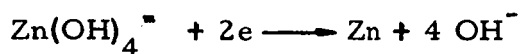Figure 4.   Diagram of Electrolytic Cell, Showing Placement of Electrodes

A.   Calomel electrode inside Luggin capillary.
B.   Zinc working electrode.
C.   Platinum counter electrode isolated with fritted glass disc.

In the Ag/Zn battery, the over-all reactions at the zinc electrode are:

<u>Anodic dissolution (discharge)</u>

(i) $Zn + 2OH^- \longrightarrow Zn(OH)_{2(Solid)} + 2e$

(ii) $Zn(OH)_2 + 2OH^- \longrightarrow Zn(OH)_{4(Solution)}^=$
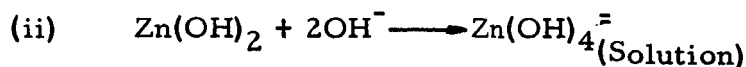
<u>Cathodic deposition (charge)</u>

$$Zn(OH)_4^= + 2e \longrightarrow Zn + 4\ OH^-$$

The calculated standard reversible potential for this couple at room temperature is equal to -1.216 Volt vs. S. H. E. or -1.460 Volt vs. S. C. E. The measured open circuit potentials of the systems used in the present study, using both the S. C. E. and a hydrogen electrode in the same solution as reference electrodes, have been consistently about 150 mV more cathodic than the standard value. This difference is thought to be accounted for by the increase in the activity of OH^- over that of the standard conditions, and possibly also to an unusually low activity coefficient for zincate at the relatively high concentrations employed (i. e. , greater than 0. 1 $\underline{M}$).

Each of the above processes is strictly potential dependent. One of the most important parameters in electrochemistry is the overpotential, which is the difference between the operating potential and the reversible value. It is this parameter that controls the kinetics of an electrode process. Variables such as the concentration, real electrode area and temperature, while they affect the actual rate of the process, are not as important as the potential which governs, for example:

a.   the structural nature of an electrodeposit and,

b.   areas of the surface which, during electrodissolution will be the first to be oxidized.

It was, therefore, decided for the initial phase of this research, to employ a method in which potential was the controlled variable and current was recorded as a function of time.

The potential was maintained constant using a Wenking potentiostat. Current voltage curves were recorded in the potential range 0 to -2 Volts (European Sign Convention). During dendrite growth the potential was held at 50 mV increments, at values cathodic to the reversible potential. The current was noted as a function of time, generally for periods up to one hour, after which time the dendrites were of the order of 1 mm in length.

2.2.2   Current-Voltage Curves

Potentiostatic current-voltage curves were obtained at room temperature in the following solutions:

(w) % KOH	Molarity of Zincate
30	0.1, 0.2, 0.3
40	0.1, 0.2, 0.3
44	1.1 (saturated solution)

The current-voltage curves exhibited the characteristic shape seen in Figure 5 which shows a curve obtained in a saturated solution of zincate in 44% KOH. This concentration approximates that employed in some Ag/Zn batteries. The figure shows both a forward (cathodic direction) and reverse (anodic direction) sweep at a sweep rate of 36 mV/min: the potential is quoted versus the S. C. E.

The following regions were evident:

    a.   0 to ~ -1300mV. The only process taking place here is the anodic oxidation of zinc to form initially solid $Zn(OH)_2$ and ultimately $Zn(OH)_4^=$ (soluble zincate). The current density in this region was fairly constant at a value around 30 mA/cm^2 during both the forward and reverse sweeps.

    b.   Between -1300 and -2000 mV the forward and reverse sweeps were found to be distinctly different.

        1)   Forward sweep

            Between -1300 and -1350 mV, current oscillations were observed. These were not uniform and apparently had no fixed frequency or amplitude. The frequency was in the range of 0.5 to 5 sec.$^{-1}$

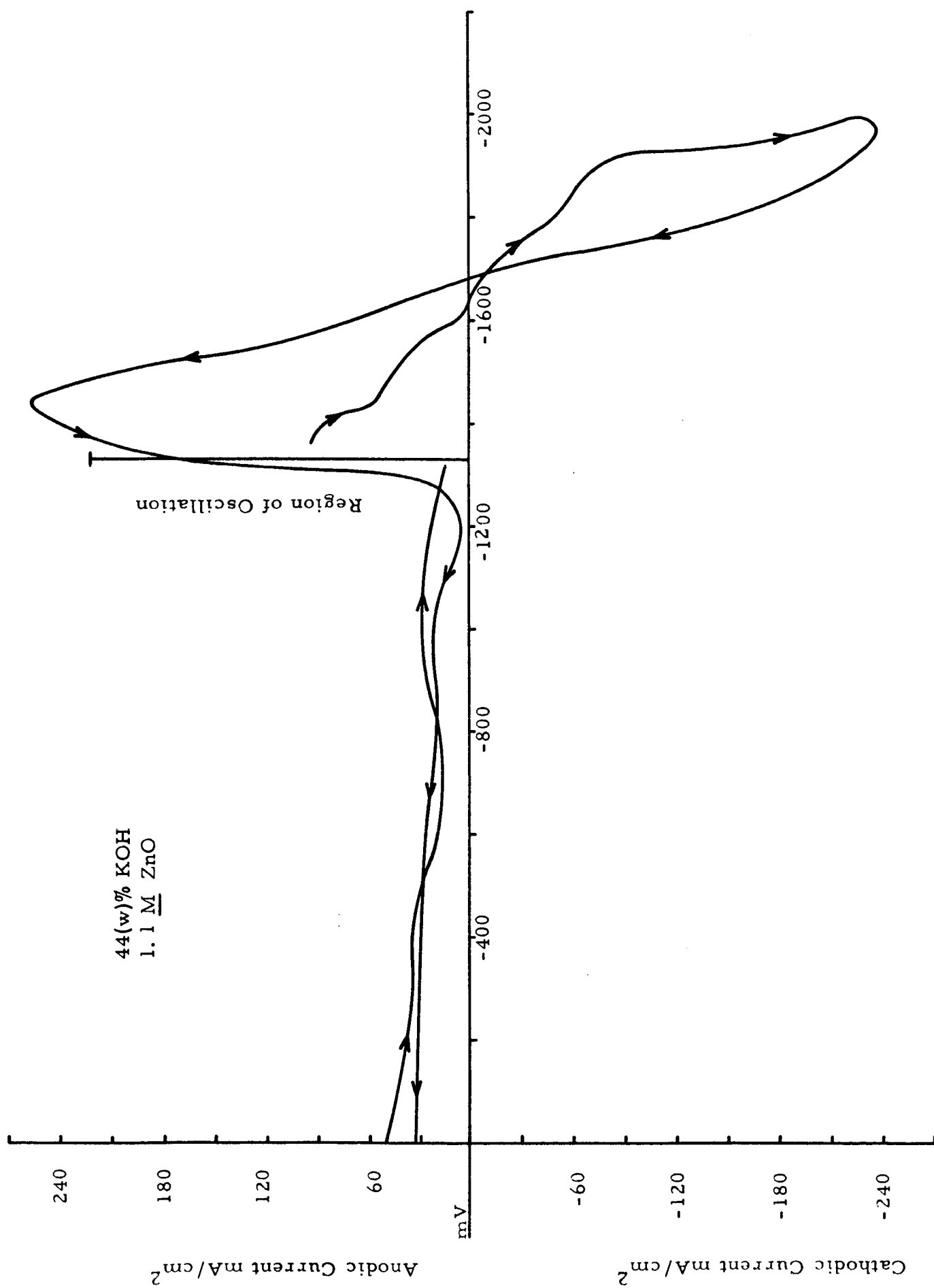Figure 5. Potentials vs. SCE. Sweep Rate 36 mV/min.

44(w)% KOH
1.1 $\underline{M}$ ZnO

Region of Oscillation

Anodic Current mA/cm^2

Cathodic Current mA/cm^2

mV

240   180   120   60

-60   -120   -180   -240

-2000   -1600   -1200   -800   -400

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and the amplitude varied between a few mA/cm^2 and
220 mA/cm^2. There is no clear explanation for
these oscillations but they have been observed in a
variety of different systems and are usually
associated with the rapid formation and dissolution
of passive layers.

Between -1350 and -1600 mV the current remained
anodic, decreasing gradually from about 100 mA/cm^2
to zero at the apparent reversible potential (-1600 mV).
The fact that a larger current was observed during
this section of the sweep indicates that the effect of
passing through the oscillation region is to cause a
roughening of the surface. (Anodic oxidation
currents would be expected to be closely governed
by surface roughness.) As the potential was made
more cathodic, beyond the reversible value
(-1600 mV), the current was cathodic as a result of
the electroreduction of zincate from the solution
and also in small measure the reduction of the solid
zinc hydroxide on the electrode surface, which had
been formed on the anodic part of the sweep. The
fact that the current in this region increased as the
potential was made more cathodic is due to the fact
that as the dendrites grow, the roughness factor
increases and, therefore, the cathodic reduction
current becomes larger. This is supported by the
fact that at the lower concentrations (i. e., 0.1 to
0.3M in zincate), the current increase was much
less evident because, (1) the number of coulombs
passed was lower and, (2) at the lower concentra-
tions the current was found to be partially
diffusion-controlled (i. e., affected by stirring) and,
therefore, not so much a function of the real
electrode area. At a potential of about -1900 mV
hydrogen evolution started to take place together
with zinc reduction. The potential of the hydrogen
electrode in this system was recorded as -1108 mV
vs. S. C. E. indicating that the hydrogen over-
potential was about 800 mV.

2)   Reverse Sweep

On the return sweep, the current between -2000 and
-1675 mV (the apparent reversible potential), was
greater than on the forward sweep. This is

attributed to the fact that at these low sweep rates and the high concentration of zincate, dendrite formation is beginning, resulting in an increase in the real electrode area. Between -1675 and about -1300 mV, a large maximum was observed. The presence of such a maximum is easily explained: During the cathodic section sufficient dendrites have been formed to cause a very much increased roughening of the electrode surface which results in a larger anodic oxidation current. Eventually, at around -1300 mV the dendrites have been removed and the surface is now relatively smooth again and the current decreases correspondingly.

2. 2. 3 Current/Time Curves

Figure 6 shows a current/time curve recorded during dendrite growth at -1700 mV in 44% KOH containing 1. 1 $\underline{M}$ zincate. As expected, this current increased with time owing to the fact that the dendrites increased the effective electrode area. Similar behavior was found in all the solutions studied and at all potentials where dendrites were grown. This was the case even for the low concentrations (0. 1$\underline{M}$) of zincate where the reaction is diffusion-controlled: After dendrites have grown sufficiently, i. e. , to a length greater than the approximate diffusion layer thickness, ~5 x 10^{-2} cm, the current ceases to be proportional to the apparent electrode area and is, instead, governed by the real electrode area (of the dendrites). In this case the diffusion layer can be thought of as following the contours of the surface.

2. 3 GROWTH OF DENDRITES

Initial studies of the growth of dendrites on a smooth zinc substrate, have been aimed at a qualitative description of the dependence of general features upon concentrations of electrolyte and zincate and upon potential during growth. The mode of dissolution of the dendrites upon subsequent anodization (corresponding to the discharge cycle of the battery) has also been observed.

Dendrites were grown in each of the electrolyte/zincate concentration combinations tabulated in the previous section on current-voltage characteristics, and usually at each of the following potentials (vs. S. C. E.) in each system:

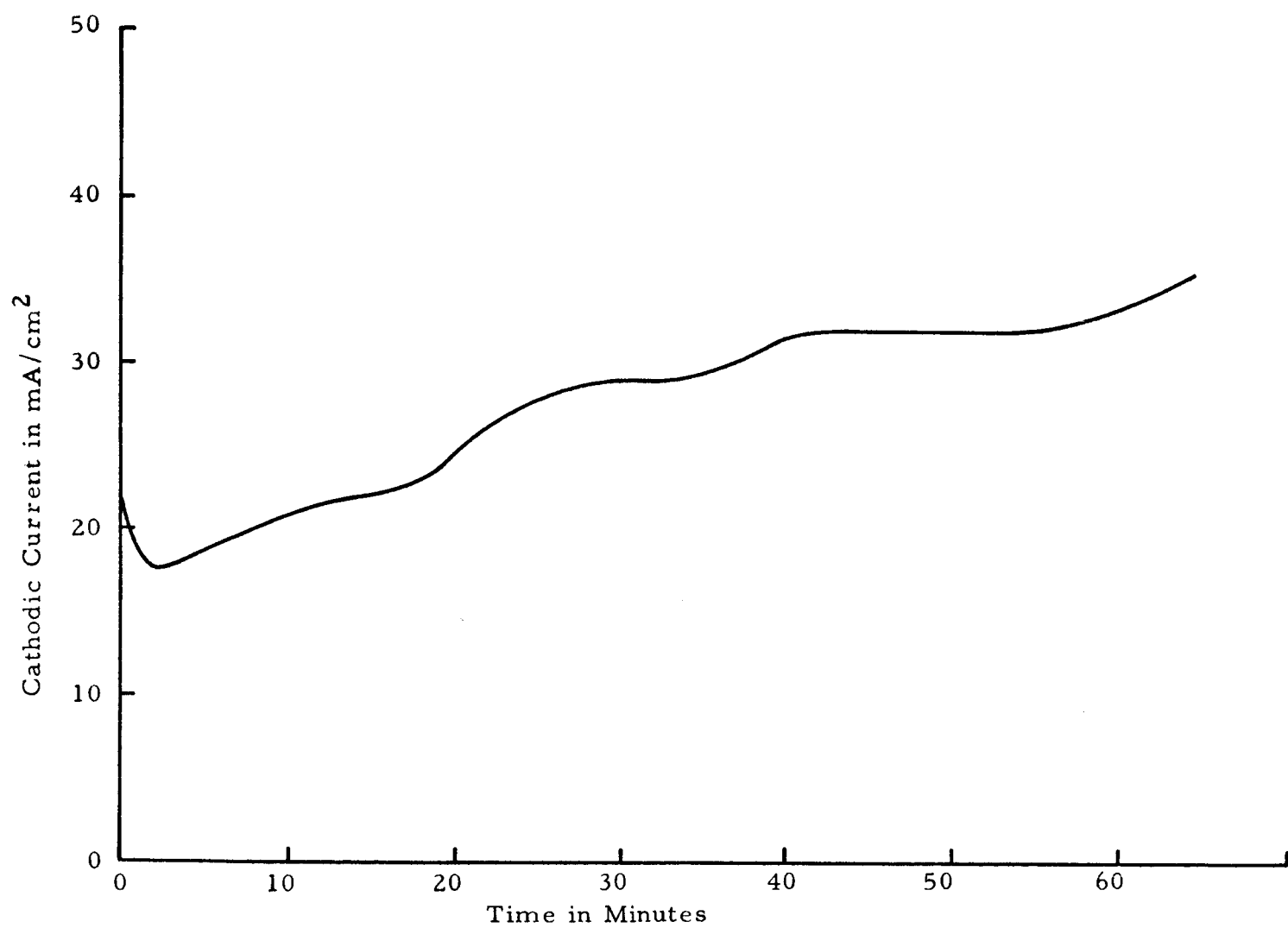-1650, -1700, -1750, -1800, -1850, and -1900 mV.

Figure 6. Cathodic Current as a Function of Time at -1700 mV (S. C. E.) in 44(w)% KOH, 1.1 $\underline{M}$ ZnO

This range covers the potential region between the reversible potential of the zinc system and the hydrogen-evolution potential on the zinc.

The initial dendritic growth on each particular zinc electrode was made on the mechanically polished zinc surface; subsequent depositions were made on the exposed polycrystalline surface left by complete dissolution of the previous deposit. No trends were exhibited in the results that could be attributed to this difference; however, this variable will be more closely controlled and studied during the next period, along with other variations in the nature of the substrate.

Intermittently during each growth cycle the deposition current was noted; this provided the current-time curves whose features have been described in the previous section. Photographs were taken at intervals, so that a complete relationship between current, time, and appearance (including extent of propagation) was established.

Figure 7 shows a photograph of a stage micrometer (0.1 mm per division) placed in the position normally occupied by the zinc electrode. This establishes a scale for the measurement of the dendrites.

The most important finding in the work thus far is that the shape and texture of the dendrites is markedly affected by the potential at which they are grown. The trend in growth characteristics with potential described below has been exhibited in all combinations of hydroxide and zincate concentrations. No effect at all has been established for the former, and the primary effects of the zincate concentration are upon rate of growth (current) and rate of propagation, and only secondarily upon the nature of the growth. The current at a given potential of growth varies widely with the concentration of zincate (as expected for a diffusion-controlled process) without affecting the nature of the growth. The form of this dendritic growth is therefore not, as is sometimes stated in reports on battery testing, due to the charging current, but rather to the potential that the zinc electrode is forced to assume as a result of imposing a particular charging current in a system containing a particular concentration of zincate.

When deposition was carried out at potentials only slightly cathodic to the reversible value (i. e. , within about 50 mV), a "mossy" growth of dendrites was invariably obtained. This type is illustrated by Figure 8. This deposit was grown in 30(w)%KOH/0. $1\underline{M}$ Zn(OH)$_4$$^=$ at -1600 mV (10 mV cathodic to the experimental reversible potential under these conditions).
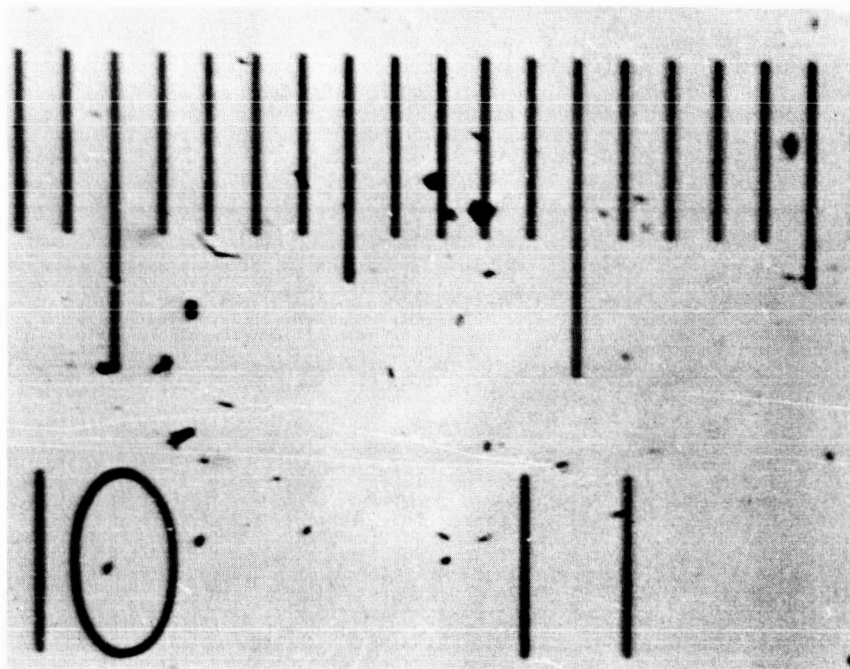
Figure 7. Photograph of Stage Micrometer at
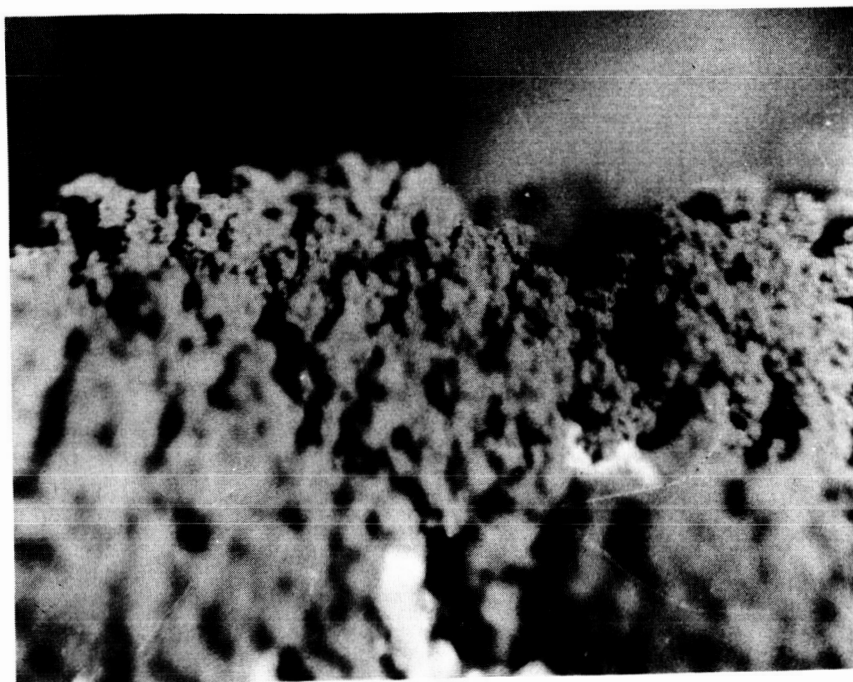Position of Zinc Electrode. 0.1 mm per division

Figure 8. Mossy Dendrites (Grown at -1600 mV
in 30(w)% KOH/0.1 $\underline{M}$ Zn^{+2})

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Deposition around 100 mV cathodic to the reversible potential produced characteristic "pine tree" dendrites such as those shown in Figure 9. This deposit was made in 30(w)% KOH/0.3$\underline{M}$ Zn(OH)$_4^=$ at -1700 mV. Deposition at potentials between -1600 and -1700 mV was sometimes observed to produce a hybrid of the "mossy" and "pine tree" forms.

Figures 10 and 11 were chosen to illustrate two points. Both photos are of the same deposit, grown in 30(w)% KOH/0.2$\underline{M}$ Zn(OH)$_4^=$ at -1750 mV. As a result of the still more cathodic potential, compared to that for Figure 9, they show greater definition of crystal structure and a higher degree of branching. In addition, the sequence illustrates a mode of branching: Figure 11 was taken 15 minutes after Figure 10. In Figure 10 there is an edge view of a dendrite grown at the top of the field and slightly to the left of center. Visible on the left face of this dendrite are two small nuclei. The lateral propagation from these nuclei is clearly visible in Figure 11.

Figure 12 illustrates still another variation in dendritic form which we have chosen to call "acicular". Its basic similarity to the "pinetree" form is apparent; however, its tendency is to grow from fewer nucleation sites and to propagate along the spike axis rather than to add to the bulk of the existing structure. The deposit in Figure 12 was grown at -1800 mV in 30(w)% KOH/0.1$\underline{M}$ Zn(OH)$_4^=$. The acicular modification is thought to be more associated with simultaneous hydrogen evolution on the electrode, than with the potential itself. The effect could be due to either the reduction of water at the metal surface as a process competing with discharge of zincate, or to the effect of the hydrogen bubbles on mass transfer of zincate to the zinc surfaces. The evidence for the association of acicular dendritic growth and hydrogen evolution is that, while the practical hydrogen evolution potential under the conditions of Figure 12 is about -1800 mV (i. e. , the same as that at which Figure 12 was produced), at higher concentrations of zincate (e. g. , 1.1 $\underline{M}$ in 44% KOH) the normal pine tree form persists at this potential, and the acicular form is not developed until around -1950 mV; the practical hydrogen evolution potential in the latter system is also displaced cathodically to approximately this potential. (In practice the evolution of hydrogen is quite apparent visually and it was necessary to interrupt the current temporarily to take a clear photograph of the dendrites in Figure 12.)

2.4   ANODIC DISSOLUTION OF DENDRITES

At the end of each growth experiment, the dendrites were removed from the electrode surface by anodic dissolution, usually at about -1400 mV (200 mV anodic to the reversible potential). Two features of this

Figure 9. Pine Tree Dendrites (Grown at
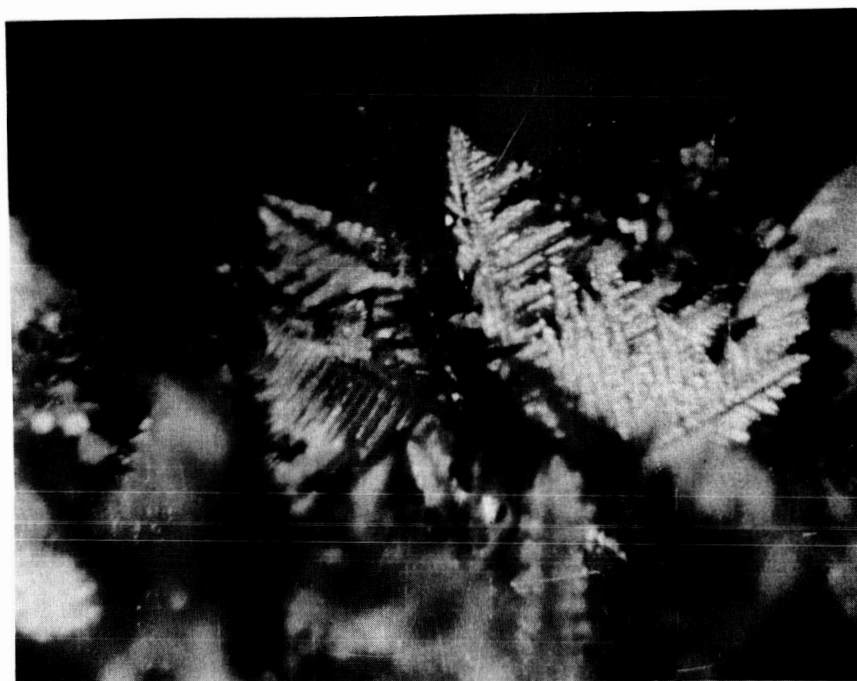-1700 mV in 30(w)% KOH /0. 3 $\underline{M}$ $Zn(OH)_4^=$)

Figure 10. Highly Branched Pine Tree Dendrites
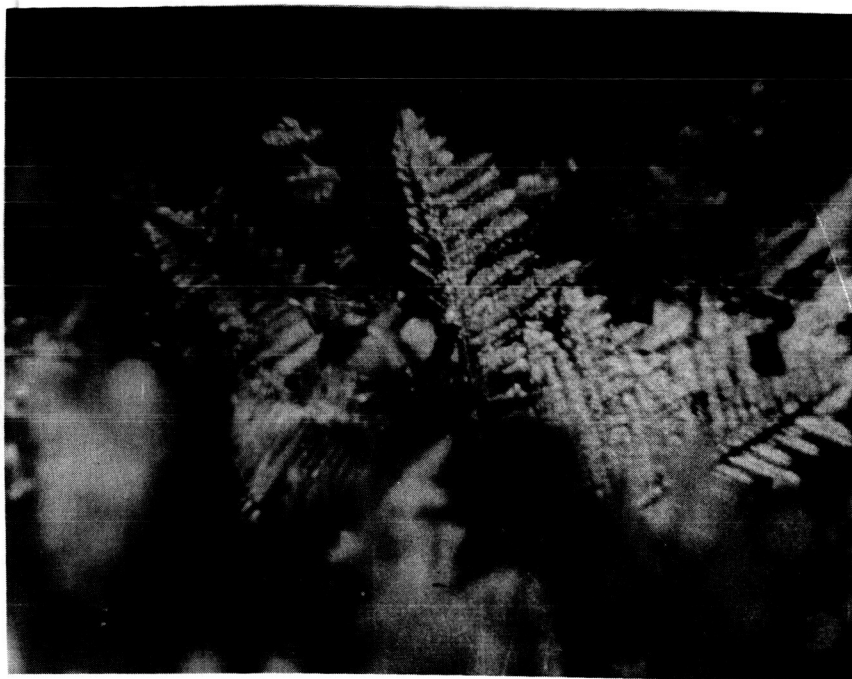(Grown at -1750 mV in 30(w)% KOH/0. 2 $\underline{M}$
$Zn(OH)_4^=$)

Figure 11. Dendrites of Figure 10 After 15 Minutes Additional Growth

Figure 12. Acicular Dendrites (Grown at -1800 mV in 30(w)% KOH/0. 1 $\underline{M}$ Zn(OH)$_4^=$)

process have been observed that may have significance for practical battery operation. First, it was observed that the entire dendrite formation immediately blackened upon application of the dissolution potential and that hydrogen evolution occurred on the dendrites simultaneously with their dissolution. This black surface was also observed during current-voltage scans on smooth zinc in the potential region anodic to the reversible potential. In the potential region where oscillations in current have been described to occur, the black film flickers across the surface synchronously with the low current point in the oscillation. Beyond the oscillation region, (i. e. , in the completely passivating region of potential) the black surface persists on the electrode. These observations imply that the blackened surface is characteristic of a passivated electrode, where the color is thought to be due to excess zinc in the passivating hydroxide (or oxide) layer. We have observed that this surface is an extremely active form of zinc capable of spontaneously displacing hydrogen at visible rates from the electrolyte even while standing at open circuit (i. e. , about -1600 mV). This is striking since hydrogen is normally evolved from smooth zinc or the dendrites only at much more cathodic potentials (as noted above, -1800 mV or more). Zinc is commonly considered a metal exhibiting a very high "overpotential" for the hydrogen evolution reaction. The thermodynamic potential necessary for hydrogen evolution in this system is approximately -1100 mV. Thus, in the case of smooth zinc or "bright" dendrites as observed in this work, the "overpotential" amounts to about 700-800 mV. On the smooth (but blackened) electrode, then, this overpotential is effectively reduced to at most 500 mV and, on the blackened dendrites during dissolution at -1400 mV, to no more than 300 mV. This mechanism of activation of the zinc for the hydrogen evolution reaction could be partly responsible for the excessive gassing rates encountered toward the end of deep battery discharge or on short circuit at the end of discharge, since the potential of the zinc electrode does tend to more more and more anodic into its passivation region under these conditions.

Figure 13 illustrates the evolution of hydrogen during dendrite oxidation, and also demonstrates another important aspect of the dissolution process, which is that the extended dendrite growth away from the main surface is not reduced appreciably until the very last stages of oxidation. Rather, most of the current goes toward reducing the thickness of the individual dendrites. (In the photograph, the plane of the electrode is just below the field of view.) This suggests that, unless the dendrites are completely oxidized during discharge of the electrode, a superstructure remains which will enhance the rate of dendrite propagation normal to the electrode surface during the next charging cycle. In this manner dendrites may build through the inter-electrode space in a battery during repeated charge/discharge cycling. Regrowth on top of a partially oxidized dendrite structure has not as

Figure 13.   Appearance of Dendrites Near the Completion of Anodic Dissolution at -1400 mV.   (Plane of the electrode is just below the field of view.)

yet been attempted to substantiate this suggestion, but will be done during the next reporting period.

2.5 NEW TECHNOLOGY

No new methods or techniques have been developed as a result of the studies conducted during this reporting period.

SECTION III - PROGRAM FOR THE NEXT REPORTING PERIOD

Considering that no gross effects on dendritic form have been found due to either the concentration of electrolyte or the concentration of zincate, most of the investigation during the next period will be conducted in 40-44 w/o KOH with zincate concentrations at or near the saturation value (approximately 1. 0 $\underline{M}$). These experimental conditions should be close to those encountered during charging of a Ag/ Zn battery.

One type of measurement that is important is the rate of propagation of the dendrites in the direction normal to the plane of the zinc electrode. Such a quantity would be most reasonably quoted in the units of length of growth (maximum) per unit of Zn deposited (e. g. , mm/coul). The values of this rate can then be plotted against time to illustrate how the rate of propagation varies with stage of growth.

The rate of propagation is a significant parameter in the evaluation of the tendency of the dendritic deposit to short circuit the plates of the battery. It is felt that these rates may be considerably different for the various types of dendrites described in this report, and that therefore, the tendency to short will depend on the potential at which growth occurs. The evaluation of rates of propagation will include determinations of how regrowth on partially oxidized dendrites, corresponding to shallow discharge, affects the over-all rate of propagation on cycling.

Furthermore, two additional parameters will be brought into the study. These will be the nature of the zinc substrate including compressed zinc plaque electrodes of a commercial type, and temperature (over the approximate range 0 - 50°C). It will be determined how these parameters affect the general conclusions of the work done to date, if at all, and in particular how temperature and substrate variations affect the rates of propagation.

SECTION IV - CONCLUSIONS AND RECOMMENDATIONS

Results to date seem to indicate that the form of zinc dendrite is dependent on deposition potential. It does not seem likely that control of potential alone will eliminate dendrite growth. The nature of the dendrites is not significantly affected by KOH or zincate concentrations.

Preliminary results indicate that dendrites are not entirely removed during discharge of the zinc.

It is recommended that further studies should include such variables as temperature, and the form of the initial zinc surface. Further studies should be made of the effect of repeated charge-discharge cycles in the growth, disappearance and re-growth of dendrites.